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GEOCHEMISTRY.—*Clays and soils in relation to geologic processes.*[1] CLARENCE S. ROSS, U. S. Geological Survey.

The importance of clays and soils can hardly be overemphasized, for no materials play a wider and more varied role in geologic processes than do the clays and related minerals. These have in the past been so little understood, indeed were long looked upon as such hopeless materials, that geologists tended to avoid the problems on which they had a bearing and missed much of the information that they were capable of giving after intensive study. However, advances in the knowledge of clays and the development of efficient techniques for studying clay and soil materials have already contributed to this branch of geology, and the way has been opened for new advances. This paper presents and illustrates by specific studies certain geologic problems on which clay and soil materials have a bearing—problems some of which have been clarified in the course of mineralogic research and others on which tentative conclusions have been reached.

During the meetings of the First International Soil Congress in Washington in 1927, soil mineralogy was an almost totally neglected subject, but interest began to grow almost immediately afterward. However, the writer presented at these meetings a paper that was based on studies in the laboratories of the United States Geological Survey in which it was pointed out that many soils are characterized by minerals of the montmorillonite group. These studies have since been carried forward in collaboration with others, including Sterling B. Hendricks, of the U. S. Department of Agriculture. Contributions have come from many sources in this and other countries. Some of those making noteworthy contributions are Paul F. Kerr, of Columbia University; John Gruner, of Minnesota; W. P. Kelley and associates, of California; Grim and associates, of the Illinois Survey; C. E. Marshall, of Leeds, England, but more recently of the University of Missouri; Harrison and Hardy, of the Imperial College of Tropical Agriculture, Trinidad; Nagelschmidt, of Rothemstead; Hofmann and his associates, in Germany; Edelman and Noll, of Germany; and Favejee, in Holland.

Work remains to be done on the mineralogy of clays, but the studies have progressed until we have a fairly adequate knowledge of the minerals involved, their compositions, and their physical properties. The full details of clay mineralogy are unnecessary here, but a few of the minerals whose properties have a bearing on geologic relationships may be briefly mentioned.

Three main groups of minerals are found among the clay minerals: the kaolinite group, the montmorillonite group, and the group variously called hydrous mica, bravaisite, or illite. All have a platy or micaceous structure. Kaolinite and halloysite are the only minerals of the kaolinite group that are known to be present in soils, but dickite occurs in hydrothermal deposits. These three minerals differ in the arrangement of the lattice sheets but not in chemical composition, and have the following common chemical formula:

[1] Address of the retiring President of the Geological Society of Washington delivered at the 611th meeting of the Society on December 9, 1942. Published by permission of the Acting Director of the U. S. Geological Survey. Received April 8, 1943.

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Kaolinite
Halloysite } $Al_2Si_2O_5(OH)_4$
Dickite

This formula indicates that kaolinite is characterized by a high alumina-silica ratio. The valency is completely balanced within the crystal structure, and hence no balancing ions (exchangeable bases) are present. There is little or no tendency for iron, magnesium, or other ions to proxy aluminum in the crystal structure. Kaolinite appears to be the stablest of the clay minerals.

The members of the montmorillonite group, typically developed in bentonite, have an extremely wide range in chemical composition. Clays are commonly assumed to be essentially hydrous aluminum silicates, and yet within this single group ferric iron, magnesium, and even chromium may proxy aluminum in part or even completely, and a wide variety of ions, including lithium, ferrous iron, manganese, and nickel, may be present in minor amounts. Ions with a valency of 1, 2, or 3 may take the place of trivalent aluminum, and aluminum may take the place of at least one silicon ion out of four, thus playing two distinct roles in the crystal structure. The substitution of even small amounts of bivalent magnesium for trivalent aluminum, and of trivalent aluminum for tetravalent silicon, results in a valency deficiency within the crystal lattice. This deficiency is compensated by ions that are held between the crystal sheets and are the so-called exchangeable bases; that is, members of the montmorillonite group are characterized by the presence of cations which may be exchanged for other cations on treatment with water or other solvent carrying the second cation. The position of these cations between the crystal sheets permits base exchange without affecting the crystal structure of the clay. This stochiometric exchange of cation for cation distinguishes base exchange from adsorption, although the two are commonly confused. These bases are associated with the interlayer water (the water film present between each molecular sheet), the association that gives bentonites and related clays their peculiar physical properties.

Experimentally, almost any base or hydrogen may be exchanged for bases occurring naturally. Those occurring most widely are calcium, which is almost completely exchangeable, and sodium, which is usually exchangeable but not always completely so. Small amounts of potassium, magnesium, and even aluminum may be replaceable, as is hydrogen, which gives the clay an acid reaction. These ions differ greatly in their relative ease of replacement, which is represented by the following series:

$$Li < Na < H < K < Mg < Ca$$

This relation indicates the reason for the preferential fixation of calcium in most montmorillonite even in the presence of sodium.

The dominance of replaceable calcium provides a readily available source of that element in soils characterized by montmorillonite minerals. The preferential fixation of calcium also has a particularly favorable effect on soil texture in that it promotes flacculation, whereas sodium tends to bring about extreme colloidal dispersion.

In the formulas below, the ions occupying octahedral positions within the crystal structure (those proxying aluminum) are grouped together within the first parentheses. Silicon, which occupies tetrahedral positions, follows and is also enclosed in parentheses if partly proxied by aluminum. The component ions are expressed as decimal fractions where necessary in order to keep the total of those in tetrahedral positions at the constant value of 4, making all the formulas directly comparable. The replaceable ion is placed above the ion that it balances, the two being connected by an arrow. A discussion of minerals of the montmorillonite group may be preceded by discussions of pyrophyllite and talc, two minerals related to the clay minerals, although differing markedly in physical properties. Their formulas are as follows:

Pyrophyllite $(Al_2)\cdot(Si_4)\cdot O_{10}\cdot(OH)_2$
Talc $(Mg_3)\cdot(Si_4)\cdot O_{10}\cdot(OH)_2$

The chemical formulas quoted below will serve to illustrate the relations within the montmorillonite group, although they are not intended to represent the ranges in

composition fully. Complete representation would require at least eight formulas together with rather detailed discussions, but those included will illustrate geologic relationships. In pyrophyllite and talc there are no appreciable substitutions of the other ions for Al or Mg or of Al for Si; the valency is completely balanced within the crystal structure, and these minerals, like kaolinite, show little or no base exchange.

Two minerals of the montmorillonite group showing characteristic substitution of ions are

$$\text{Montmorillonite } (Al_{1.67}\overset{\uparrow}{Mg}_{0.33}\overset{Na_{0.33}}{}) (Si_4)O_{10}(OH)_2$$

$$\text{Hectorite } (Mg_{2.67}\overset{\uparrow}{Li}_{0.33}\overset{Na_{0.33}}{}) \cdot Si_4 \cdot O_{10} \cdot (OH,F)_2$$

The foregoing formula of montmorillonite differs from that of pyrophyllite in that 1 Al ion out of six is being proxied by Mg. The valence deficiency that has been introduced into the crystal lattice by this substitution of a bivalent for a trivalent ion is balanced by Na, which is situated between the sheets. In the formulas this replaceable base is given as Na, but it is commonly Ca, plus small amounts of other bases. The montmorillonite represented here, if containing in addition the normal content of interlayer water, differs from pyrophyllite only in containing about 3.23 percent of MgO and 2.55 of Na_2O. This small change in composition has introduced the property of base exchange, and the interlayer water that brings about the markedly different physical properties of these minerals.

The relations between hectorite and talc are similar to those between montmorillonite and pyrophyllite. The substitution of about 1 percent of univalent Li for bivalent Mg, together with the Na required for balancing the valency, has again made the difference between talc and hectorite with remarkably complete colloidal dispersion.

The clays of the montmorillonite group in which Al proxies Si in essential amounts have been called beidellite. The formula given below represents closely the clay from the type locality, Beidell, Colo.:

$$\text{Beidellite } (Al_{1.46}\overset{+3}{Fe}_{.50}Mg_{.08}) (\overset{\uparrow}{Al}_{0.36}Si_{3.64}\overset{Ca_{0.16}}{})O_{10}(OH)_2$$

Here ferric iron and a small amount of Mg take the place of part of the Al, so this formula is more repesentative of soil-forming members of the group than other formulas presented. The exchangeable base is represented as Ca rather than Na, and the ions in octahedral positions exceed 2 by a small amount.

Formulas representing two other members of the group are given below:

$$\text{Saponite } (Mg_3) (\overset{\uparrow}{Al}_{0.33}Si_{3.67}\overset{Na_{0.33}}{})O_{10}(OH)_2$$

$$\text{Nontronite } (\overset{+3}{Fe}_{2.00}) (\overset{\uparrow}{Al}_{0.33}Si_{3.67}\overset{Na_{0.33}}{})O_{10}(OH)_2$$

In both of these formulas Si is being proxied by Al and is balanced by Na between the lattice sheets.

Within the same crystal structure there may be substitutions of other ions for Al in the octahedral group, and also of Al for Si in the tetrahedral group. Where the trivalent ions, Al^{+3} and Fe^{+3}, are dominant in the octahedral group, the number of ions in that group is close to 2 but may exceed that number slightly, and where bivalent ions such as Mg are dominant, their number is close to 3 but can not exceed that number. Three octahedral positions are available but are not necessarily all occupied. In none of these formulas has the highly variable water been included; it would, if necessary, be represented by $(+nH_2O)$.

The members of the bravaisite group require further study, but they are known to be widely distributed. They have a relatively small base-exchange capacity, and in some of their properties are intermediate between micas and montmorillonite. In the micas and bravaisite the potassium lies between the crystal sheets, forming bonds that tie sheet to sheet, and hence is locked in a nonexchangeable position, in contrast with the exchangeable bases of montmorillonite, which are held on only a single surface in a manner that permits their ready displacement.

The bravaisite type of mica is not well

enough known to justify more than a general formula to represent its range of composition, but its relation to the true micas can be represented as follows:

Muscovite $K(Al_2)\ (AlSi_3)O_{10}(OH)_2$

Bravaisite $\frac{K}{2}\ (Al, Fe^{+3}, Mg)_2(Al, Si)_4O_{10}(OH)_2$

Fe and Mg are present in subordinate amounts in bravaisite but are commonly present in greater amounts than in true muscovite. The K has been represented as one-half of that in micas, but it may range down almost to zero. A typical formula for bravaisite would be

Bravaisite $\frac{K}{2}\ (Al_{1.65}\overset{+3}{Fe}_{0.15}Mg_{0.30})\ (Al_{0.50}Si_{3.50})O_{10}(OH)_2$

An unusual clay mineral, but one forming extensive deposits of fullers earth in the Florida-Georgia region, has been called altapulgite. This is characterized by a fibrous rather than a platy structure and seems to be related to the so-called mountain leather (paligorskite). The seemingly very specialized conditions that produced so unusual a sedimentary material present a real problem, but the high content of magnesium tells something of the genetic environment.

The opallike, noncrystalline clay material known as allophane may be present in some soils.

A few of the physical and chemical factors that are most important in controlling clay formation should be mentioned. The alteration of any parent material to a clay or soil aggregate takes place in a physical-chemical system whose varied factors, taken one at a time, are approximately known. There are, of course, many varying sets of conditions that may dominate the development of a clay material, but in general it is the combined effect of difficultly evaluated interrelationships, more than the unknown effect of any one factor, that introduces the complexity that characterizes many clay problems.

In reality there is only one fundamental factor in clay formation—the chemical character of the reacting system. This may be divided into two secondary factors: the chemical character of the parent material and the chemical character of the altering solutions. These factors will be most conveniently illustrated by specific studies to be mentioned later. The other factors are complex and varied but serve only to impede or accelerate reactions in the system. Varying physical conditions such as permeability affect the access of solutions and hence the rate, but not the final character, of the reaction. Time is a factor only in that it permits reactions that proceed with extreme slowness.

Organic materials have a marked effect on soil texture, water retention, and fertility, but the chemical effects are in general due to their reducing action (essentially the reduction of ferric to ferrous iron) and to the solution and removal of bases by organic acids. In humid and especially in cool humid climates, and in swamps where peaty and lignitic materials collect, the effect of organic materials is a dominant factor; in desert regions, or where there is rapid oxidation of organic materials, their effect may be small or absent.

Living organisms play an important role in soil processes, some of them modifying physical relations, as when they facilitate the access of air or water to the system. Bacteria and other micro-organisms play a very important role, and their use of such materials as oxygen, nitrogen, and sulphates contributes chemical factors to the soil- or clay-forming system.

The mineralogic, chemical, and physical processes discussed above provide a basis for a general outline of the manner in which they interact to form the three different groups of clay minerals—montmorillonite, bravaisite, and kaolinite.

The four distinctive relationships of members of the montmorillonite group may be restated: the essential role of magnesium in the chemical composition, the entry of iron in all proportions into the crystal structure, the replaceable bases, and the interlayer water between each molecular sheet. Montmorillonite and other members of the group have been synthesized in the presence of alkalies and alkaline earths, but montmorillonite has been formed under the widest range of conditions in the presence of mag-

nesium. Other work indicates that alkaline conditions may not be absolutely necessary, especially if magnesium is present, but montmorillonite probably does not form under acid conditions.

Experimental evidence does not cover the effect of other bases, but chemical composition and conditions of formation indicate their effect rather clearly. Ferric iron enters the crystal structure of members of the montmorillonite group but forms no part of the kaolinite structure; hence the presence of ferric iron in the clay-forming system favors the formation of montmorillonite. Ferrous iron plays the same role as magnesium in silicate minerals, so it too would tend to favor the formation of montmorillonite. Even where little or no ferrous iron enters the crystal structure, its mere presence, owing to its higher solubility, would increase the availability of iron in the clay-forming system. The presence of organic materials in association with suitable bacteria gives reducing conditions, and, therefore, reduction or even the absence of active oxidation, would tend to favor the formation of montmorillonite. The lithium of hectorite would exert the same effect as magnesium. Other bases including calcium and sodium tend to give alkaline conditions and in this way promote the formation of montmorillonite.

Chemical composition, experiments on synthesis, and the interrelations of ions as revealed by X-ray studies of crystal structure, combine to explain the tendency for solid rock and detrital materials rich in ferromagnesian minerals and calcic feldspars, to alter to montmorillonite.

The soils of the Piedmont region are under investigation by L. T. Alexander and associates of the Department of Agriculture, and some of the interpretations by S. B. Hendricks of the relations between parent rock and the resulting clay minerals are about to be published. This interpretation shows that the soils derived from Triassic diabase are in general composed essentially of montmorillonite, whereas some of the other ferromagnesian rocks of the region under similar physical and climatic conditions have weathered to kaolinitic soils. It seems evident that in the diabase the ferromagnesian minerals and feldspar break down together, releasing iron (part of it ferrous), magnesium, alumina, and silica, giving conditions favorable for the formation of montmorillonite or beidellite. In these other rocks the ferromagnesian minerals break down first, the magnesium is removed by solution, and the iron is either removed or is altered to oxides. The feldspars break down later, and in the absence of magnesium, and with the iron absent or effectively isolated from reaction by oxidation, kaolinite forms.

The alteration of basaltic rocks to montmorillonite under suitable conditions has been described by Hosking (1940), who has made a study of the origin of a group of Australian soils. According to him, "It is evident that granite types of parent material will weather to kaolinite or halloysite under a very wide range of climatic conditions . . . In the case of basaltic soils, the internal moisture conditions . . . appear to play an important part in determining the mineral clay type formed . . . The first two profiles (developed on basalts) are characterized by good drainage conditions, allowing of complete oxidation, whereas the third is subject to a certain degree of waterlogging. The soils with good internal drainage, whether formed on granite or basic rock, are both characterized by a clay mineral of the kaolinitic type . . . In the clay where waterlogging is apparent and free oxidation restricted, montmorillonite is formed to the exclusion of kaolinite. The absence of crystalline iron (oxide) minerals, despite the high content of iron in the clay is undoubtedly due to the restriction in oxidizing conditions, a fact reflected in the greenish color of the clay."

Glacial materials are composed of feldspars, other aluminous and ferromagnesian silicates together with sedimentary materials derived from calcareous beds, shales, and sandstones. On weathering aluminum, silicon, iron, magnesium, calcium, and alkalies are released and a chemical system favorable for the development of montmorillonite is formed.

Lamar, Grim, and Grogan (1938) give

the following description of the soils formed from glacial materials: "Gumbotil is derived from glacial till by weathering . . . Gumbotil does not occur on glacial drift as young as the Wisconsin drift, but is common on the older drifts—the Illinoian, Kansan, and Nebraskan. It formed under conditions of poor drainage usually just below the soil layer over broad, flat upland tracts . . . The conversion of till to gumbotil in nature involves oxidation, leaching of carbonates, and chemical decomposition of the silicate materials . . . The original till contained large amounts of clay minerals of the illite group and in general the processes of weathering have tended to remove alkali, particularly potassium, and to alter the illite minerals to those of the montmorillonite group."

Bentonites, whose essential mineral is montmorillonite, have a world-wide distribution and show no observable relation to climatic zones. Their derivation from glassy volcanic ash has long been established and needs no discussion. This ash seems to have fallen on land, in fresh-water lakes, in saline lakes, and in marine embayments. The failure to show a clear mineralogical relationship to these various environments is not easily explained, but perhaps leaching was in some places a subsequent process brought about by ground water after burial. Such a genetic environment has been indicated by the work of Bramlette on the bentonites in the Monterey shales of California.

The exact composition of the volcanic glass from which bentonite was derived is known for only a few occurrences, but the associated minerals show that it was most commonly the latite type of rock—that is, essentially a feldspathic rock. More rarely it was rhyolitic. In a few occurrences the resulting bentonite is known to be higher in magnesium than the glass from which it was derived, indicating that magnesium was derived from magnesium-bearing marine or ground waters. Marine waters are slightly alkaline and ground waters are alkaline or neutral.

The need for more detailed information about the mineralogic relations of the bravaisite group has been mentioned, and the same is true of their geologic relations. Minerals of this group are dominant materials in marine shales, and in soils derived from such shales. Over wide areas, especially in the east-central United States, they are major soil-forming materials.

The Ordovician of the eastern half of the United States contains bentonitic beds that are characterized by a clay mineral of the bravaisite type; it therefore differs from the more normal montmorillonite type of bentonite. So far as known, this type of bentonite is confined to the Ordovician, a restriction in occurrence that has not been explained. The wide distribution—from Georgian Bay, Canada, on the north to Alabama on the south, and from Pennsylvania on the east to Minnesota and Missouri on the west—is one of its interesting features. Over these wide areas, the bravaisite bentonites contain over 5 percent of potash, or about one-half of that of muscovite.

Some, if not all, of the Ordovician bentonites represent marine deposits, and it seems probable that these, like the marine shales, derived their potash from ocean waters. However, some of the montmorillonite bentonites that are essentially potash-free contain marine fossils and must have formed in marine embayments, although we do not know that leaching took place in the presence of ocean waters.

Geologists have long known that where potassium in solution in river, ocean, or saline lake comes in contact with clay materials there is a preferential fixation of potassium. Potassium salts are commonly minor constituents of such waters and sodium salts are dominant, even where the two were originally supplied in nearly equal amounts. Spencer and Murata in an unpublished paper have shown that preferential adsorption of potassium from sea water is not an adequate explanation of this relationship.

The gradual inversion of montmorillonite to bravaisite or micalike minerals seems to offer an explanation of this preferential fixation of potassium and the dominance of potassium minerals in marine deposits. The formulas representing mineral compositions indicate the chemical similarity between the mica minerals and montmorillonite, and X-ray work shows that the crystal struc-

tures of the two minerals are very similar. There is the physical difference that the potassium of micas is linked between the sheets in a nonreplaceable condition. In montmorillonite, sodium and calcium are readily replaceable, but experiments on soils show that potassium, even where initially replaceable, gradually becomes nonreplaceable. It seems probable that under favorable conditions potassium comes to occupy positions tying sheet to sheet—that is, positions characteristic of the micas. Thus potassium may gradually become fixed at the expense of replaceable bases.

Kaolinite is the common end product resulting from several geologic processes and is especially characteristic of areas of deep and thorough weathering and of areas where leaching has been unusually effective. Its occurrence as an end product of such rigorous geologic processes is no doubt related to its high degree of stability and its common association with the most stable minerals. These are commonly quartz, iron oxides, and hydroxides, and in some occurrences aluminous hydroxides. The red or red-brown color imparted to kaolinitic soils by associated free iron oxides is in contrast to the greenish, blue-gray, or pale-yellow colors of montmorillonite in which ferric iron forms a portion of the crystal structure.

The association of kaolinite with iron oxides in many deposits shows that it formed under oxidizing conditions. In other deposits, from which iron had been removed, the kaolinite formed in the presence of organic materials which gave reducing conditions. Reduction and solvent action by organic acids favor the removal of bases, including magnesium, calcium, and alkalies as well as ferrous iron. The tendency for acids derived from organic materials and oxidizing sulphides to form kaolinite is well known. It seems evident, therefore, that the removal of bases from the clay-forming system is the essential factor in kaolin formation and that the kaolinizing action of acids is due to their efficiency in removing bases rather than to their effect as acids. Long-continued leaching in essentially neutral waters may remove all bases, except where active oxidation inhibits the removal of iron. Feldspar pegmatites in the southern Appalachian region have been altered to kaolinite to a depth of a hundred feet or more. The pentration of acid solutions to such depths during the course of weathering is improbable, and such kaolin bodies have undoubtedly been due to the leaching action of essentially neutral waters.

The common association of iron oxides and kaolinite should be considered in connection with the earlier statement that iron may favor the formation of montmorillonite. The effect of ferrous iron in promoting the formation of montmorillonite, as already pointed out, would be destroyed by oxidation. Under extreme oxidizing conditions iron would be leached from silicate minerals and immediately redeposited as oxide; in this form it would be removed from the reacting system almost as effectively as when removed by solution.

Soils formed from limestone are commonly characterized by kaolinite, and since this mineral has a low base exchange capacity, such soils are commonly deficient in calcium. On the other hand, volcanic ash low in calcium will alter to montmorillonite containing essential calcium.

Harrison, and later Hardy and Follett-Smith (1931) who cited the work of Harrison, studied the soils of British Guiana. The former author reports: "Under tropical conditions, the katamorphism of basic and intermediate rocks at or close to the water table, under conditions of more or less perfect drainage, is accompanied by the almost complete removal of silica, and of calcium, magnesium, potassium, and sodium oxides leaving an earthy residuum of trihydrate (in its crystalline form gibbsite). . . . This residuum is termed primary laterite. . . . The process of primary lateritisation is succeeded by one of resilication. . . . Under tropical conditions acid rocks do not undergo primary lateritisation, but gradually change . . . to more or less quartziferous and impure kaolins . . . On well drained mountain plateaux, where rainfall is very high and more or less continuous throughout the year, primary laterite appears to be permanent . . . On badly drained low-lying areas on the other hand, primary laterite appears not to be permanent but gives rise to argillaceous earths . . .

"During the passage upwards by capillary attraction in dry seasons when evaporation exceeds rainfall, the silica-bearing solutions derived from underlying rock forms surface films of moisture in the spongy primary laterite where some of the silica reacts with some of the finely divided gibbsite to form a hydrated aluminum silicate principally a crystalline kaolin."

Alexander, Hendricks, and Faust (1941) report that, "Gibbsite has been shown to be a component of a number of soil colloids from continental United States. It is a major component of some of them.

"The primary weathering products of norites, amphibolites, an epidote greenstone schist, a diabase, and muscovite-biotite schists, have been shown to contain gibbsite . . . Where silica is being liberated by mineral weathering in close proximity to the gibbsite, resilication to kaolinite takes place."

The bauxite deposits of Arkansas, the Gulf coastal region, and the valley of Virginia show an invariable association with the more abundant and widespread kaolin beds from which they are believed to have been derived. The relations in all these areas indicate that the formation of these deposits is not comparable to the usual picture of laterization, where ferric iron is concentrated together with aluminous minerals. In most of these areas no iron-free parent material is available for the formation of white, commonly very pure kaolinite, as where kaolin is derived from feldspar pegmatites. In widely separated areas there is an association of kaolinitic materials with lignitic beds, or with horizons characterized by widespread swampy conditions. The relations between bauxite and lignite beds in Arkansas has been discussed by Behre (1932). Almost without exception ferrous iron carbonate has been deposited in underlying or closely associated beds. Siderite concretions are not rare within the beds themselves. Thus iron has been removed, a removal normally possible only after reduction; ferrous iron carbonate is a constant associate; and there is a widespread association with swamps or lignitic beds, which provide a most efficient source of reducing agents and organic acids that dissolve and remove bases. The control that this group of interrelations has exercised in the production of the kaolin beds in these particular regions seems obvious. This, however, leaves many problems that require intensive study, in particular the genetic relations between the bauxite and the kaolin beds.

In the presence of mineralizing solutions or volcanic vapors, the pressure, temperature, and concentrations commonly favor the formation of ferromagnesian silicates, feldspars, and micas more commonly than clays. In the later stages of activity, however, as temperatures decrease there is an increased tendency for clay minerals to form and clays have been reported from numerous veins and other mineral deposits, all three types of clay materials having been identified. Dickite, the hydrothermal member of the kaolinite group, is very widespread and is commonly associated with vein quartz. Bravaisite is probably reported as sericite in most lists of minerals as the two are very difficult to distinguish. If montmorillonite is observed only in thin section, it too may be mistaken for sericite; however, its low mean index of refraction clearly distinguishes it.

The relative temperatures of formation of these three clay groups are not definitely known, but perhaps dickite forms at higher temperatures than montmorillonite. The common association of dickite with quartz and a seeming absence of associated ferromagnesian silicates is no doubt significant, and the absence of iron and magnesium may be necessary for its formation. On the other hand, it is evident that montmorillonite forms in the presence of the bases, ferric-iron and magnesium, and under alkalic if not alkaline conditions. The alteration of the feldspar of pegmatites to kaolinite under leaching conditions has been mentioned, but a number of pegmatites have been described in which hydrothermal alteration has produced montmorillonite. In these, introduction of bases has predominated over their removal, and montmorillonite has been produced.

The genetic processes revealed in two in-

teresting occurrences of clay minerals illustrate the relations between kaolinite and montmorillonite. Studies of the hot springs of Yellowstone National Park by Allen and Day indicate that acid waters are the result of oxidation of hydrogen sulphide near the surface, and that the primary waters or vapors are all alkaline in depth.

Fenner (1936) in his detailed studies of the materials encountered in drill holes put down in selected parts of the hot-spring areas of the park, gave special attention to the relation of these materials to depth, pressure, and the chemical character of the escaping vapors. He says: "The effect of acidity is thus apparent in the formation of kaolinite as far down as 95 feet, . . . at greater depths the alteration produced beidellite only." That is, below the zone of acid solutions a clay of the montmorillonite group formed. The highest pressure measured was 277½ pounds at a depth of 246½ feet, where the temperature was 205° C. Thus a mineral of the montmorillonite group may form at rather high temperatures and pressures in the presence of alkaline solutions. Fenner observes that pyrite commonly accompanies beidellite in the Yellowstone materials.

The conclusions by Fenner about the origin of clay minerals at Yellowstone coincide with relationships at Magnet Cove, Ark. (Ross, 1941). Steam-shovel operations connected with rutile mining have shown the existence of a volcanic neck filled by an agglomerate made up of various rock types and enclosed in a matrix of clay minerals. Abundant rutile and pyrite are associated with these materials. A nearly pure feldspathic rock shows various degrees of alteration to montmorillonite. The matrix material around rock fragments was originally glassy volcanic ash, but this has been altered to montmorillonite, which has been in part later altered to kaolinite. The relationships indicate that volcanic waters and vapors carrying bases and rich in sulphides, rose through the porous agglomerate altering both feldspar and glass to montmorillonite. It seems evident that as volcanic activity waned, these sulphide-bearing vapors were in part condensed and oxidized in contact with air. This resulted in sulphuric-acid-bearing solutions, which percolated back into the porous agglomerate, partly altering the montmorillonite to kaolinite.

The foregoing outline presents a much generalized picture of soil-forming processes in which many of the factors discussed have been qualified as trends or tendencies. Detailed studies of individual occurrences will no doubt show many apparent exceptions, which will be cleared up only by intensive geologic work involving correlation between mineral composition and the physical and chemical factors that interacted to produce the clay material.

The relationships between many different parent rocks and their products of weathering need to be studied. Information is especially needed about the clay minerals in fine-grained sedimentary rocks, and the resulting product, where these are exposed by erosion and themselves undergo weathering. The relative effects of leaching in the presence of solutions of differing chemical character have not been determined in adequate detail. Alternate wetting and drying probably is more destructive than either continued aridity or humidity, but this question has never been fully investigated. Intermediate or transitory products may intervene between the parent rock and the end product, and may influence the character of that product. The effect of base exchange on the quality of ground water is being studied, but the effect of salts carried in solution upon the sedimentary materials is too little known. Is the clay or soil the result of reactions in a single physico-chemical system or have there been changes that make it the result of several genetic episodes? Is the clay material in equilibrium with its environment or not; that is, to what extent may clay minerals be in a metastable condition? Has there been admixture with materials from several sources that developed under distinct environments? What were the conditions of final disposition, was it in fresh or salt water? How have all these processes been modified by associated organic materials? Numerous soil types from many parts of the world have been described, and soil specialists

have given particular attention to the different horizons of the soil profile, and those geologists particularly interested in soil problems are under obligation to consider this work and understand the geologic significance of soil types and soil profiles. Much of this needed information will be attained only by detailed studies of selected areas where the greatest number of controlling factors are determinable; but also much more may be determined and recorded as incidental results during the course of general geologic studies of a region. This is needed because the science of soil geology is in many ways in the early stages in which the mere accumulation of information by workers in many fields is necessary as a basis for future progress. Here are problems for the mineralogists, geologists, soil specialists, chemists, and physicists—in particular geologists and physical chemists.

Dr. W. P. Kelley, of the University of California, one of our most far-seeing soil scientists, presented as a part of a symposium on clays at the University of Chicago in 1941 a paper entitled "Modern clay researches in relation to agriculture" (1942), which should interest all geologists. In this he said: "A knowledge as to the kind of clay minerals found in soils bids fair to throw important light on soil formation processes, that is, on soil genesis . . .

"Modern researches on the clays are, therefore, placing the subject of soils on a new footing. They have served to emphasize the close relationship between soil science and geology and mineralogy . . . There is simply no point where you can separate geological from soil processes . . .

"That clay research is drawing soil science into closer contact with geology is one of its important by-products. In my opinion the closer the cooperation between soil workers and geologists the better. In fact I look upon several of the important phases of soil science as aspects of geology."

Dr. Kelley has made himself the leading advocate among soil scientists of the necessity of the geologic and mineralogic approach to many soil problems and of the inadequacy of purely chemical methods. However, he and other leading soil workers feel, seemingly not without some reason, that geologists have not given all the help for which their training fits them.

Clay studies are not without their bearing on the broader problems of geology—the problems of those geologists who are not primarily interested in soils and related materials. The promptness with which clay materials react to changes in environment is a measure of the information they may hold. Clays respond to acid or to alkaline conditions, to swamps or to aridity, to oxidizing or reducing conditions, to fresh water or to marine deposition, to the presence or to the absence of organic materials. No one can see all the possibilities that may come of any research, but some of the results may be suggestive.

The bentonites have told us much. These clays are the only record of the ash showers that fell so widely in Ordovician seas. They are also evidence of the volcanic activity that ringed the Gulf of Mexico in Cretaceous and Tertiary time, with a dozen or more ash showers recorded in the clays of Mississippi. They seem to present evidence that certain embayments were of fresh or at most brackish water, whereas other embayments of the same general region were marine. Clays have presented very definite evidence as to the chemical character of mineralizing solutions and no doubt will present much more as they are intensively studied.

The clays hold a story that will grow as we know them better. Should we not heed the earnest plea of men like Dr. Kelley that geologists accept as their own some of the problems of soils?

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PHYSICS.—*The scientific significance of ferromagnetism.*[1]

FRANCIS BITTER, Massachusetts Institute of Technology. (Communicated by R. E. GIBSON.)

Half a century or so ago theoretical and experimental investigations were undertaken that revealed the main facts about ferromagnetism. On the one hand, they made possible the formulations of ideas that are basic in an understanding of the subject and, on the other hand, led to technical developments that made possible the enormous electrical industry of today. It would be interesting to follow both of these developments simultaneously, but I have chosen to concentrate on the scientific rather than on the engineering aspects of the subject. Ewing, Weiss, and Curie showed us that a ferromagnetic substance owed its peculiar properties to the interaction of elementary magnets of atomic dimensions, that these interactions were not entirely of magnetic origin, and that the transition from ferromagnetism at low temperatures to paramagnetism at high temperatures was not a real change of phase, as melting for instance, but a new sort of transition associated with a discontinuity of specific heat rather than a latent heat. Weiss showed that to a first approximation, at any rate, ferromagnetism could be understood as a special case of paramagnetism in which Langevin's fundamental equation relating magnetization to the dimensionless quantity $\mu H/kT$ had to be modified only by assuming that the field acting on each elementary particle was not the externally applied field alone, but the resultant of this field and an internal field resulting from the interaction of the elementary magnets with each other and on the average proportional to the intensity of magnetization itself. Thermodynamically the results achieved were sound and satisfying, except perhaps that stress and strain tensors were omitted from the theory, and all phenomena related to magnetostriction and thermal expansion were omitted. These are, however, not fundamentally important and can be incorporated into the theory at the expense of simplicity. Statistically, the results were not satisfactory. Although the Boltzmann constant appears, this is due only to the incorporation of the theory of paramagnetism, and the real problem of interpreting the atomic interactions is avoided altogether by the simple assumption of an internal field. From the point of view of atomic physics, one important result was achieved: namely, the specification of the order of magnitude of atomic magnetic moments. On the other hand, the actually observed values of Curie temperatures of the order of 1,000° K. could not be explained on the basis of known interatomic fields, and the origin of these fields was a major mystery for many years.

One last item remains to be mentioned to complete the picture prior to the advent of the quantum theory and more recent developments in atomic physics. The Weiss theory, because of its simplifying assumptions regarding atomic interactions and the internal field, predicted spontaneous magnetization of an entire sample to saturation at all temperatures below the Curie point. This was completely contrary to fact, and left unexplained the origin of hysteresis, and all the phenomena related to magnetization—of such great technical impor-

[1] The twelfth Joseph Henry Lecture delivered before the Philosophical Society of Washington at its 1210th meeting on December 19, 1942. Received April 13, 1943.